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COMPLETE SPECIFICATION.

Reduction of Viscosity of Water-Soluble Non-Ionic Cellulose Ethers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for reducing the viscosity of water-soluble non-ionic cellulose ethers and to low viscosity cellulose ethers produced by the process.

The viscosity of cellulose ethers i.e. the viscosity exhibited by solutions of the ethers, is usually controlled by controlling the degree of degradation of the cellulose from which the ether is subsequently prepared. This is conveniently effected by allowing soda cellulose, prepared in the first stage of cellulose ether manufacture, to be oxidised by atmospheric air or chemical oxidising agents, such as hydrogen peroxide while it is stirred at normal or elevated temperatures.

This method of viscosity control has the disadvantage that the cellulose degradation effected is not uniform. Consequently low viscosity grades of cellulose ether—for example those having a viscosity of less than 50 centipoises in 2% aqueous solution at 20° C.—when thus prepared, contain portions which are excessively soluble in and are consequently difficult to isolate from the strongly alkaline liquors in which they are prepared.

We have now discovered that in the preparation of low viscosity water-soluble non-ionic cellulose ethers it is advantageous to first prepare an ether of higher viscosity than that desired and to subsequently treat this material to reduce its viscosity to the desired value.

In accordance with the invention the viscosity of a water-soluble non-ionic cellulose ether is reduced by treating it, without substantial dissolution, with an aqueous solution of hydrogen peroxide, the duration and temperature of such treatment being controlled in accordance with the amount of reduction in viscosity desired. The viscosity of the product obtained depends on the initial viscosity, the concentration of the hydrogen peroxide solution, and the temperature and duration of the treatment.

The method of the invention permits more accurate control of the viscosity of the product to be effected than was generally possible with the methods hitherto used and by its use process conditions which involve low viscosity cellulose ethers being slurred in strongly alkaline reaction liquors may be avoided, thereby obviating the difficulty of isolating the ether from such liquors.

In this Specification the term "water-soluble non-ionic cellulose ethers" means non-ionic ethers which can be dissolved in some aqueous medium but not necessarily in all aqueous media. It therefore includes those which, while being insoluble in neutral solutions, are soluble in alkaline solutions. Generally such ethers include those having a degree of substitution of between 0.1 and 2.3.

In one convenient manner of carrying the invention into effect a substantially dry mass of water-soluble non-ionic cellulose ether or a mass of such ether moistened with a liquid in which it is insoluble is sprayed evenly with an aqueous solution

of hydrogen peroxide and thereafter subjected t heat treatment sufficient to effect the required viscosity reduction. This heating may conveniently be carried out in a drying oven so that the heat treatment and evaporation of water and volatile liquids may be effected simultaneously. While all the water-soluble non-ionic cellulose ethers may be thus treated this method is particularly advantageaus for the treatment of those ethers such as hydroxyethyl cellulose which are soluble in hot water and which consequently cannot be treated in a hot aqueous slurry.

In another convenient method of carrying out the invention the cellulose ether may be suspended as a slurry in a liquid in which it is insoluble and the aqueous oxidising agent added. This liquid may conveniently be a mixture of alcohol and water having an alcohol content sufficient to prevent any substantial gelling of the ether. For the treatment of ethers which are soluble in water at room temperature but insoluble in hot water the liquid is conveniently water maintained above the temperature at which gelation of the ether occurs (the gel point). This latter method may be advantageously employed in the treatment of a variety of cellulose ethers including methyl-, ethyl-, ethyl methyl-, hydroxyethyl methyl-, hydroxyethyl ethyl-, hydroxypropyl methyl, and hydroxypropyl ethyl-cellulose.

If ethyl alcohol is also present with the mass of ether being treated, little reduction in viscosity takes place until the temperature is raised sufficiently to evaporate off the alcohol, but after the alcohol is removed the peroxide becomes effective.

Treatment of cellulose ether in accordance with the invention may be carried out under alkaline conditions, but it is more effective under neutral or nearly neutral conditions. Consequently it is preferred to effect treatment at a *p*H of between 5 and 9.

The invention is further illustrated by the following examples in which all parts are by weight.

The viscosity of the cellulose ethers recorded was determined by the method of British Standard 188 (1957) using a U-tube viscometer. All the viscosities were measured at 20° C.

EXAMPLE 1.

7.5 parts of hydroxypropyl methyl cellulose containing 0.2 hydroxypropyl and 1.8 methyl groups per anhydroglucose unit having a viscosity of 2800 centipoises (cps.) and a gel point of 65° C. in 2% aqueous solution were suspended as a slurry in 60 parts of water at 75° C. One part of 100 vols, strength hydrogen peroxide (approximately 30% H_2O_2 by weight) was added to the slurry and the temperature was maintained at 75° C. for 2 hours after which time the hydroxypropyl methyl cellulose was isolated. The viscosity of the hydroxypropyl methyl cellulose in 2% aqueous s lution was found to be 240 cps.

EXAMPLE 2.

5 parts hydroxypropyl methyl cellulose containing 0.2 hydroxypropyl and 1.8 methyl groups per anhydroglucose unit having a viscosity of 2170 cps. in 2% aqueous solution and a gel point of 65° C. were suspended in 40 parts of water at 100° C. One part of 100 vols. strength hydrogen peroxide was evenly mixed into the slurry and the temperature maintained at 100° C. for 1 hour. The hydroxypropyl methyl cellulose was then isolated and its viscosity was found to be 18 cps. in 2% aqueous solution.

EXAMPLE 3.

10 parts of hydroxypropyl methyl cellulose containing 0.2 hydroxypropyl and 1.8 methyl groups per anhydroglucose unit having a viscosity of 17000 cps. in 2% aqueous solution and a gel point of 90° C. were suspended as a slurry in 80 parts water at 95° C. One part of 100 vols. strength hydrogen peroxide was mixed evenly into the slurry and the temperature maintained at 95° C. for 2 hours. The hydroxypropyl methyl cellulose was isolated and found to have a viscosity of 7500 cps. in 2% aqueous solution.

EXAMPLES 4—13

Examples 4—13 were carried out to illustrate the effect of (a) concentration of hydrogen peroxide, (b) times of treatment and (c) temperature of treatment on the viscosity reduction of hydroxypropyl methyl cellulose. The details of these examples are set forth in Table 1. In each of the examples 25 parts of hydroxypropyl methyl cellulose containing 0.2 hydroxypropyl and 1.8 methyl groups per anhydroglucose unit having a viscosity of 4070 cps. in 2% solution and a gel point of 65° C. were suspended as a slurry in 200 parts of water at the temperature indicated. The indicated quantity of 100 vols. strength hydrogen peroxide was then added and the temperature maintained constant during the treatment time, after which the hydroxypropyl methyl cellulose was isolated and its viscosity in 2% aqueous solution determined. These viscosity values are given in the last column of Table 1.

Examples 4—6 illustrate the effect of the concentration of oxidising agent, Examples 7—10 illustrate the effect of the duration of treatment and Examples 11—13 illustrate the effect of temperature.

TABLE 1.

Example	Temperature	Parts H_2O_2 added	Duration of Treatment	Viscosity of Product 2% aqueous Soln.
4	100° C.	0.83	1 hour	282 centipoises
5	"	4.15	1 "	23 "
6	"	8.3	1 "	20 "
7	"	0.83	15 minutes	1888 "
8	"	"	30 "	963 "
9	"	"	45 "	735 "
10	"	"	1 hour	282 "
11	70° C.	4.15	30 minutes	1430 "
12	85° C.	"	30 "	554 "
13	100° C.	"	30 "	191 "

EXAMPLE 14.

25 parts of ethyl hydroxyethyl cellulose containing 1.2 ethyl and 0.2 hydroxyethyl groups per anhydroglucose unit having a viscosity of 2585 cps. in 2% aqueous solution were suspended as a slurry in 200 parts of water at 95—100° C. 0.83 parts of 100 vols. strength hydrogen peroxide were added and the slurry was maintained at a temperature of 95—100° C. for 30 minutes. The cellulose ether was isolated and dried and found to have a viscosity of 296 cps. in 2% aqueous solution.

EXAMPLE 15.

25 parts of methyl cellulose containing 1.9 methyl groups per anhydroglucose unit having a viscosity of 2685 cps, in 2% solution were suspended in 200 parts of water at 95—100° C. 0.83 parts of 100 vols. strength hydrogen peroxide were added and the temperature of the slurry was maintained at 95—100° C. for 30 minutes. The cellulose ether was isolated and found to have a viscosity of 306 cps. in 2% aqueous solution.

EXAMPLE 16.

25 parts of methyl cellulose containing 1.9 methyl groups per anhydroglucose unit having a viscosity of 5780 cps. in 2% aqueous solution were suspended in 200 parts of water and treated with hydrogen peroxide in the manner described in Example 16. The viscosity of the isolated product was 637 cps. in 2% aqueous solution.

EXAMPLE 17.

75 parts of hydroxyethyl cellulose containing 1.5 hydroxyethyl groups per anhydroglucose unit having a viscosity of 7382 cps. in 2% aqueous solution were sprayed, whilst mixing in an incorporator, with 53 parts of a solution containing 3 parts of 100 vols. strength hydrogen peroxide in 32.5 parts ethanol and 17.5 parts water. The material was then placed in an oven at 80° C. for 4 hours after which time the volatile liquids had evaporated from the hydroxyethyl cellulose and the viscosity of the latter was found to be 158 cps. in 2% aqueous solution.

The above procedure was repeated using as the spray liquid 56 parts of a solution containing 6 parts of 100 vols. strength hydrogen peroxide, 32.5 parts ethanol and 17.5 parts water. The product had a viscosity of 44 cps. in 2% aqueous solution.

WHAT WE CLAIM IS:—

1. A process for reducing the viscosity as hereinbefore defined of water-soluble non-ionic cellulose ether as hereinbefore defined which comprises treating the cellulose ether, without substantial dissolution, with an aqueous solution of hydrogen peroxide, the duration and temperature of the treatment being controlled in accordance with the amount of reduction in viscosity desired.

2. A process in accordance with Claim 1 wherein a mass of cellulose ether, either dry or moistened with a liquid in which it is insoluble, is sprayed evenly with a quantity of aqueous solution of hydrogen peroxide insufficient to effect any substantial dissolution of the ether and is thereafter subjected to sufficient heat treatment to effect the required viscosity reduction.

3. A process in accordance with Claims 1 or 2 wherein the cellulose ether is an ether which is soluble in both hot water and water at ordinary temperatures.

4. A process in accordance with Claim 1 wherein the cellulose ether is suspended as a slurry in a liquid in which it is insoluble and the aqueous solution of hydrogen peroxide is added to the slurry.

5. A process in accordance with Claim 4 wherein the cellulose ether is suspended in an aqueous alcohol having a sufficient alcohol concentration to prevent substantial gelling of the ether.

6. A process in accordance with Claim 4 wherein a cellulose ether which is soluble

in water at room temperature and insoluble in hot water is suspended in water maintained at a temperature above the gel point.

7. A process in accordance with Claim 6 wherein the cellulose ether is methyl, ethyl-, ethyl methyl-, hydroxyethyl methyl-, hydroxyethyl ethyl-, hydroxypropyl methyl- or hydroxypropyl ethyl-cellulose.

8. A process in accordance with any one of Claims 1 to 8 wherein the cellulose ether is treated with the oxidising agent at a *p*H of between 5 and 9.

9. A process for reducing the viscosity of water-soluble non-ionic cellulose ether substantially as described herein and as set forth in any of Examples 1 to 18.

10. Cellulose ether which has been treated in a process in accordance with any one of Claims 1 to 10.

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